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EXPERIMENTS AND OBSERVATIONS

TENDING TO SHOW

THE COMPOSITION AND PROPERTIES

OF

URINARY CONCRETIONS.

BY

GEORGE PEARSON, M.D. F.R.S.

FROM THE

PHILOSOPHICAL TRANSACTIONS.

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EXPERIMENTS, &c.

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I. *Historical Observations.*

URINARY concretions have obtained their denominations, like most other things, from their obvious properties. Accordingly, in our language, they are popularly known by the names Stone and Gravel, or Sand, from their resemblance to the states of earth so named: and we find names of the same import in other languages, such as λιθος, (ARETÆUS;) λιθιασις, (CÆLIUS AURELIANUS;) ψαμμος, (ARETÆUS;) λιθιδια, (various authors;) *Calculus*, (CELSUS and PLINY;) *Sabulum*, (various authors.) In other languages, and especially in those now spoken, it is unnecessary to notice names which have the same meaning.

The notion very generally entertained, of the nature of urinary concretions, consisted with the terms, till the last twenty years; although the experiments of SLARE, FREDERIC HOFFMAN, and HALES, long before showed that these substances commonly consist of animal matter. GALEN indeed imagined that φλεγμα, or viscid animal matter, is the basis of animal concretions; but, in his days, earth was believed to be the basis of animal matter. Alkaline medicines were, however, employed by the Greek physicians, in diseases from calculi.

The experiments of the alchemists also made it appear, that earth was only a part of the matter of concretions. It was probably the observation of the deposition and crystallization of saline bodies, which suggested the notion of urinary calculi being of the nature of tartar. Such was the opinion of BASIL VALENTINE, and after him of HOCHENER, better known by the name of PARACELUS; but, whether the latter adopted the denomination *Duelech* from its import, or from caprice, has not been explained. VAN HELMONT, a century after his prototype PARACELUS, being struck with the experiment in which he discovered the concretion of salts in distilled urine by alcohol, was led to depart from his adored master's opinion, with respect to the nature of calculi; although he acknowledges the merit of PARACELUS, in having discovered the solvent *Ludus*, (a calcareous stone also called *Septarium*,) which VAN HELMONT says is preferable to alkaline lixivium. He also says, that when the archeus spirit of urine meets with a volatile earthy spirit, and does not act in a due manner, a concretion will be formed; but, in a healthy state, although all urine contains the matter of urinary calculi, no concretion can take place, because the archeus, or vital power of the bladder, counteracts its formation.

As to the kind of earth composing calculi, the only distinction of earths, till about the last half century, was into absorbent and non-absorbent; but, since the absorbent earths were distinguished into calcareous, magnesia, and alumine or clay, the calcareous was considered to be the earth of urinary concretions; apparently however for no other reason but its obvious properties, and its extensive diffusion through the whole animal kingdom.

At length, *viz.* in 1776, the experiments of the wonderful SCHEELE were published in Sweden, but were scarcely known in this country till 1785. These experiments exploded the opinion of the earthy nature of calculi, and substituted that of their consisting of a peculiar acid, resembling the succinic, and of a gelatinous matter, without any earth. Afterwards about $\frac{1}{200}$ of their weight of lime was found by BERGMAN; which, for a cause now well known, had eluded the acuteness of SCHEELE. Although the experiments of SCHEELE were confessedly unquestionable, and were ably supported by the learned BERGMAN, some very eminent chemists, having obtained different results by their own experiments, adopted a different opinion of the composition of these concretions. The immortal, and ever to be deplored, LAVOISIER supposed these substances to consist of acidulous phosphate of lime and animal matter, many of them being partially fusible; but still it was the unrivalled SCHEELE who discovered, that the urine of healthy persons contains superphosphate, or acidulous phosphate, of lime; and who also indicated the experiment which verified his opinion, that phosphate of lime is the basis of bone.

Experiments have been likewise made, for the most part in a rather desultory way, and most of them by persons but little practiced in chemical inquiries, which at least afford evidence, that urinary concretions are very different, with respect to the proportion of the ingredients in their composition, and perhaps also in kind. M. FOURCROY, who however must not be classed with inexperienced chemists, I believe first obtained prussic acid by fire, and by nitric acid, from these concretions; and showed that they sometimes contain phosphate of ammoniac and of soda; which may be dissolved out of them by

water. M. FOURCROY also says, he found magnesia in the intestinal calculus of a horse; which calculus was a triple combination, of one part of phosphate of ammoniac, two parts of magnesia, and one of water, besides traces of animal and vegetable matter.

Dr. LINK, in a very elaborate dissertation, published at Gottingen, in 1788, on urine and calculi, concludes that urinary concretions consist of phosphoric acid, lime, ammoniac, oil, the bases of different kinds of gazes, together with the acid sublimate of SCHEELE, although he did not succeed in obtaining it.

It is a proof of Dr. BLACK'S sagacity, that he should have been able to perceive, from a few experiments, that urinary concretions consisted of animal matter and the earth of bone, before the composition of this earth was demonstrated by GAHN.

In this historical sketch it should be noticed, that alkaline substances, though used by the Greek physicians, and afterwards by the alchemical physicians, appear to have been laid aside by the regular practitioners, for a century or two preceding their revival, by the famous Mrs. STEPHENS, in 1720. Her prescription brought into vogue the theory of these medicines operating by their causticity. The successful use, by Mr. COLBORNE, of potash saturated with carbonic acid, according to the discovery of BEWLEY and BERGMAN, and the still further improvement in practice, from the use of soda, as well as potash, super-saturated with carbonic acid, by the discovery of a peculiar method by Mr. SCHWEPPE, have completely refuted the theory of the agency of alkalies on the principle of causticity.

It appears, from the preceding brief history, as well as from the confession of the latest and best writers, that the experi-

ments hitherto made, rather “afford indications of what remains to be done, than furnish demonstrations of the nature of animal concretions.” It is also too obvious to need explanation, that more efficacious and innocent practice, in diseases from these concretions, can only be discovered by a further investigation of their properties. It is with this view, as well as for the sake of chemical philosophy, that I think it my duty to submit to the Society some of the observations I have made, in the course of inquiry on this subject.

The observations which I shall now offer, are principally on a substance, which my experiments inform me is very generally a constituent of both urinary and arthritic concretions. It is a substance obtained by dissolving it out of these concretions, by lye of caustic fixed alkali, and precipitating it from the solution by acids. In this way, SCHEELLE separated this matter; but he did not consider its importance, nor of course at all investigate its properties. He does not even seem to have been aware that it was a distinct constituent part of the urinary concretion; for, when he relates the experiment of precipitating matter from the nitric solution of calculus by metallic salts, no distinction is made between the precipitations in this experiment, and that in the former; yet we can now show, that in the one case the precipitate is a peculiar animal oxide, and in the other they are metallic phosphates. As SCHEELLE obtained an acid sublimate, it has been imagined by some writers, that the precipitate by any acid (even by the carbonic) from the alkaline menstruum, was an acid; the same as that obtained by sublimation, and which, in the new system of chemistry, has been denominated *litbic acid*. The following experiments show that these substances are different species of matter.

II. EXPERIMENTS.

250 grains of a white, smooth, laminated, urinary calculus, and the same quantity of a nut-brown one, with an uneven surface, both of which were of a roundish figure, were pulverized together.* 300 grains of these pulverized calculi were triturated with three ounces and a half, by measure, or five ounces, by weight, of lye of caustic soda. The mixture became thick, and copiously emitted ammoniacal gaz. After digestion for a night, and then boiling, with the addition of five ounces of pure water, I obtained, by filtration, five ounces of clear colourless liquid. Boiling water was repeatedly poured upon the strainer, till what passed through it was almost tasteless, and remained clear, on the addition of diluted sulphuric acid.

(a) The matter remaining on the strainer, being dried, was an impalpable, white, tasteless, heavy powder, which weighed 96 grains.

(b) The five ounces of filtrated liquid, having been set apart, on standing, deposited a white, opaque, granulated, soap-like matter, from a colourless clear liquid. The liquid being decanted, the deposit was dried, and was then an opaque, brittle, soap-like matter, which dissolved readily in water, giving a clear but not viscid solution, and tasting weakly of soda. This soap-like matter weighed 280 grains.

(c) The decanted liquor, (b,) being mixed with the above filtrated liquors, on evaporation to three ounces, afforded no deposit on standing, although it was a very heavy and soapy

* The object of these experiments being principally to investigate the properties of one of the constituent parts of urinary concretions, which part was previously determined (by the test of nitric acid,) to exist in both these, it can be no objection to the experiments, that I made use of a mixture of two calculi.

liquid to the feel; but, on adding diluted sulphuric acid gradually, till it ceased to become turbid, a sediment was deposited, which was a very light, white, impalpable powder, in weight, when dried, 26 grains. The liquid from which this powder was precipitated, being evaporated, afforded nothing but sulphate of soda, and a few grains of crystals, which seemed to be phosphate of soda. There was also a blackish matter, which burnt like horn, or other animal matter, and did not leave a pink or rose-coloured matter, on evaporating the solution of it in nitric acid to dryness, but left a carbonaceous residue; whereas, the white precipitate, so treated, afforded a beautiful pink matter.

(*d*) 250 grains of the soap-like matter (*b*) being dissolved in eight ounces of pure water;

1. A little of this solution, further diluted by one ounce of water, grew milky on adding a few drops of nitric acid, but became less so on standing. On adding more nitric acid, and heating it, the mixture became quite clear: by adding a few drops of lye of caustic soda, a very slight curdy appearance took place.

2. On adding, to the same diluted solution, a little of the diluted sulphuric or muriatic acid, milkiness ensued, and remained, although the acids were added till the mixture was extremely sour. On adding lye of caustic soda, much more than to saturate the superabundant acid, the mixture became clear again; and, on adding the acids a second time, the milkiness was reproduced. It was found that the milkiness could be produced and destroyed, or clearness be produced, by the alternate addition of the acid and alkali, for an unlimited number of times. If the nitric acid however was used, at length

no milkiness could be induced. If carbonate of soda was added, in place of the caustic soda, the mixture could not be made clear.

3. Lime water was rendered turbid by this solution, but I neglected to examine the precipitated matter.

4. A little of the solution, with the addition of a few drops of concentrated nitric acid, being evaporated to dryness, sometimes a pink, and at other times a blood-red, or rose-coloured matter was left; which, by further application of fire, became black.

5. Carbonic acid, digested and shook with this solution, did not render it turbid.

6. To the whole of the remaining solution was added diluted sulphuric acid, to saturate the alkali. On standing, a copious precipitate took place, from a clear liquid; which precipitate, being washed and dried, was a mass of very light, mica-like, whitish crystals, amounting to 123 grains. It was estimated that the solution used in the Experiments 1.—5. would have produced 12 grains, and that the 30 grains of soap-like matter, (*b*,) not decomposed, would have yielded about 14 grains more.

(*e*) The precipitate, (*d*, 6.)

1. Had no taste, nor smell, and did not dissolve in the mouth.

2. About one part of it only dissolved in 800 parts of boiling water; which solution did not redden paper stained with turnsole, nor the solution and tincture of this test; neither did it change turnsole paper, reddened by acid, to a blue colour. On cooling, the greatest part of what had been dissolved was deposited, in a crystallized state, equally on the sides and bottom of the vessel. This crystallized matter had the properties abovementioned (*d*.). Boiling water was found to dissolve a much greater proportion of *urinary stone*, and also of *gravel*, than of this precipitate.

3. Lye of mild potash, or subcarbonate of potash, being dropped into the solution (*e*, 2.) with its crystallized deposit, the crystals at first seemed to dissolve; but, on standing, a great part of the matter was deposited, and the liquid remained turbid.

4. The precipitate being boiled with lye of carbonate of soda, more seemed to be dissolved than in pure water; but the solution was not clear, and, on evaporating it nearly to dryness, and pouring cold water upon it, on a paper strainer, scarcely any thing but the soda passed through with the water; the precipitate remaining behind on the paper. The result was the same, when this experiment was made with a lye of carbonate of ammoniac. The result was also the same, with water in which red oxide of mercury had been boiled; which was also boiled with this precipitate, and filtrated after cooling.

5. A little of the precipitate being triturated with quicklime, hot water was poured upon it. The filtrated liquor gave the precipitate back again, on adding muriatic acid.

6. The precipitate exposed to flame, with the blowpipe, turned black, emitted the smell of burning animal matter, and evaporated or burnt away without any signs of fusion; staining the platina spoon black.

7. Five grains of the precipitate, in half an ounce of water, were left to stand in a warm room, during the months of August and September last, without any signs of putrefaction appearing, or any obvious change taking place.

8. Twenty-four ounces of boiling water were saturated with the precipitate, and divided into six portions; from each of which, on cooling, most of it again precipitated.

The first portion, on boiling with a little lye of carbonate of

soda, (the pneumatic apparatus being affixed,) discharged no carbonic acid into lime water; but a transparent solution was produced, and, on cooling, very little was precipitated.

The second portion was, in the same manner, boiled in a little lye of caustic soda; which gave a transparent solution on cooling, without any precipitation.

The third portion being boiled with lime water, very little more seemed to be dissolved than in pure water.

The fourth portion being boiled with 4 grains of subphosphate of lime, or calcined bone, no more seemed to be dissolved on account of this addition.

Nor was more dissolved in the fifth portion, by the addition of 4 grains of phosphate of lime, made by dropping phosphoric acid into lime water.

And the result was the same with the sixth portion, to which were added 4 grains of superphosphate of lime, made by adding phosphoric acid to lime water, so as just to make a clear solution, and then evaporating the solution.

9. Urine seemed to dissolve, or at least to suspend, a greater quantity of the precipitate than mere water; so likewise did water with a little sulphate of soda.

10. The precipitate did not render solution of hard soap at all curdy; but, on adding the precipitate to solution of sulphuret of potash, it became very turbid.

11. The precipitate produced a strong effervescence, even in the cold, with nitric acid, but the fumes were not those of nitrous acid: there was a clear solution, which, on evaporation to dryness, afforded black matter, surrounded by a pink, or blood-red margin.

12. The substance, with sulphuric acid, turned black, and

emitted fumes copiously, which were scarcely those of sulphurous acid; and, on evaporation, a black mark only was left.

13. I first digested, and then boiled, in water, the precipitate with prussiate of iron; but the filtrated liquor afforded no precipitation with sulphate of iron.

14. Two drachms, by measure, of nitric acid, of the specific gravity of 1,35, were poured upon 7 grains of the precipitate. A violent effervescence took place, which was soon succeeded by a complete solution.

A few drops of this solution, being evaporated on glass, left a black mark, surrounded by a pink margin. A few drops of nitric acid being evaporated from this residue, nothing but a still less black mark, and a few red spots remained.

Nitric acid being added a third time, nothing but a black mark, still smaller, remained; which entirely disappeared, on evaporating this acid from it a fourth time.

I found that a few drops of this solution, so diluted that they did not contain the $\frac{1}{400}$, or even a much smaller part, of a grain of the precipitate, on evaporation, left a pink stain on glass.

The whole of the rest of the solution was distilled in a very low temperature, so that a drop only fell about every half-minute, till a thick brownish sediment remained, with a red margin. A similar distillation was performed, with the distilled liquor, a second time, when there remained a little whitish thick matter. On a third distillation, as before, with the distilled liquor, towards the close white fumes arose, and about half a drachm of liquid, which now remained in the retort, being left to stand, prismatical crystals, decussating each other, were formed. They had a sharp taste, but were scarcely sour;

were very soluble in the mouth, and evaporated in white fumes, leaving a very slight black stain.

15. Twenty grains of the precipitate were introduced into a tube, $\frac{1}{8}$ of an inch wide in the bore, sealed by melting at one extremity; which extremity was coated, and the tube was fitly bent for retaining sublimate, and collecting gaz. The temperature, from the fire applied, was at first very low, but was gradually increased, so as to make the coated part, containing the charge, red hot. At first, the precipitate turned black, and a little water appeared. Secondly, gaz came over, which had the smell of empyreumatic *liquor cornu cervi*. Thirdly, a brown sublimate appeared, and gaz as before, but also with prussic acid gaz. Fourthly, black matter, staining the tube, as if from tar, or animal oil. On cooling, there was found a residue, of nearly three grains, of pure carbon. The sublimate was principally carbonate of ammoniac; the rest was animal oil. The gaz discharged was nearly half its bulk, or 5 cubic inches by measure, carbonic acid; and the remaining 5 cubic inches were nitrogen gaz, containing prussic acid and empyreumatic oil.

I treated in the same manner, the same quantity of reddish crystals, deposited spontaneously from urine. The result was not very different from that of the former experiment. The gaz was more offensive, smelling like putrid urine, and the carbonaceous residue was more copious, and contained lime and phosphoric acid; at least the lixivium of it became white, on dropping into it oxalic acid; and it became slightly curdy, on adding lime water.

I treated in the same manner, some quite round and smooth

concretions, of the size of black pepper seeds. The products were the same as the former, but the gaz was still more offensive, and in smaller quantity; and the carbonaceous matter was more copious.

I, in the same way, subjected to experiment 20 grains of a nut-brown light calculus, which I had previously ascertained to contain the matter above described, which was precipitated from caustic soda by acids. The products were of the same kind as the former; but I could find no trace of phosphoric acid in the residue, which I did of lime, and the gaz was less offensive. The carbonaceous residue was not, in weight, 3 grains.

It will be proper, before I proceed further, to point out some of the more obvious conclusions from the above experiments.

1. It appears that at least one half of the matter of the urinary concretions subjected to the above experiments united to caustic soda, and was precipitated from it by acids. (II. *a—d.*)

2. This precipitate does not indicate acidity to the most delicate tests; (*e*, 2.) and, as it is inodorous, tasteless, (*e*, 1.) scarcely soluble in cold water, (*e*, 2.) does not unite to the alkali of carbonate of potash, of soda, or of ammoniac, (*e*, 3, 4.) nor to oxide of mercury, (*e*, 4.) nor to the lime of lime water, (*e*, 8.) nor decompose soap, (*e*, 10.) or prussiate of iron, (*e*, 13.) and, as its combination with caustic soda resembles soap, more than any double salt known to consist of an acid and alkali, this precipitate does not belong to the genus *acids*.

3. As this precipitate could not be sublimed, without being decomposed, like animal matter, (*e*, 15.) and also for the

reasons mentioned in the last paragraph, it cannot be the same thing as the *acid sublimate* of SCHEELE, or the succinic acid.

4. As it does not appear to be putrescible, nor form a viscid solution with water, it cannot be referred to the *animal mucilages*.

5. On account of its manner of burning in the air, under the blowpipe, (*e*, 6.) and its yielding, on exposure to fire in close vessels, the distinguishing products of animal matter, (especially ammoniac and prussic acid,) as well as on account of its affording a soap-like matter with caustic soda, this precipitate may be considered as a species of animal matter; and, from its composition being analogous to that of the substances called, in the new system of chemistry, *animal oxides*, it belongs to that genus. Its peculiar and specific distinguishing properties are, *imputrescibility, facility of crystallization, insolubility in cold water*, and, that most remarkable property of all others, *producing a pink or red matter, on evaporation of its solution in nitric acid*.*

I do not avail myself of various other conclusions in this place, because they relate especially to the agency of medicines for preventing and removing concretions; and of course do not properly fall within the views of the Royal Society.

Having found the above precipitate to be an oxide, and not, as is commonly supposed, an acid, I thought it probable that,

* It is much to be wished that we possessed equally delicate tests of the other species of animal matter, which are confounded together, although, from their obvious properties, there is reason to believe they are of very different kinds, as is the case with the matter of the brain, liver, voluntary muscles, mucus, &c. Mr. HUNTER has discovered a distinguishing specific property of pus, and one is here indicated for the oxide of urinary concretions.

like other analogous oxides, it was *acidifiable*, and I suspected that I had really rendered it into the acid state, by the nitric acid; which, in the above experiments, (*e*, 14.) had imparted oxygen to it, and thereby rendered it soluble, deliquescent, pungent, and volatile. This change also would account for the nitric solution not affording the precipitate.

In order to obtain, for examination, an adequate quantity of this supposed acid, the following experiments were instituted, with the three acids (*viz.* the oxymuriatic, the nitro-muriatic, and the nitric,) which can acidify oxides analogous to the present one.

Experiment 1. Twenty-five grains of the above animal oxide, (for so I will now venture to call it,) and three ounces of nitric acid, of the specific gravity of 1.25, were put into a retort, and the hydro-pneumatic apparatus was adjoined.

At a very low temperature, a clear solution was made. First, soon after the solution began to boil, 23 ounces, by measure, of colourless gaz came over, which were succeeded (secondly,) by white fumes, filling the apparatus, and 23 ounces more of gaz. Thirdly, a white sublimate ascended, and there was a strong smell of prussic acid. The sublimate was very readily washed out, being very soluble, and tasted pungent or sharp, but not sour. Fourthly, the distillation being renewed, more white sublimate appeared, but only 3 ounces more of gaz came over; and then the retort only contained a dark-brown solid matter.

The first portion of gaz, *viz.* 23 ounces, consisted of about equal bulks of carbonic acid and atmospherical air. The second portion, *viz.* 23 ounces, was two-thirds of its bulk carbonic acid, and the rest nitrogen gaz. The third portion,

or 3 ounces, was atmospherical air, with a little carbonic acid.

Nitric acid was poured, in the same quantity as before, into the retort. An effervescence immediately took place, which was succeeded by a transparent solution. The distillation yielded gaz of the same kind as before, but in smaller quantity, with white fumes, and white sublimate. When only about 4 drachms, by measure, of liquid remained in the retort, a little of it was evaporated; and, when reduced to a solid matter, it turned black, and took fire, leaving a carbonaceous residue; but, before this, a margin of beautiful pink matter appeared.

Nitric acid was poured, as before, into the retort, for the third time, but very little gaz ascended, and much less white fumes than before. The distillation proceeded, till about one drachm-measure of liquid remained in the retort: this being left to stand, prismatic crystals were formed in a very small quantity of liquid. These crystals did not taste sour, but sharp, and they reddened turnsole-paper. Adding a little soda to a part of them, to see whether I could form a neutral salt, I was surprised by the extrication of ammoniac. To another portion of crystals I added sulphuric acid, which disengaged nitric acid. A third portion of crystals, being exposed over a lamp, wholly evaporated, without leaving a mark behind. The remaining matter in the retort being examined, was found to be nitrate of ammoniac. It was plain that the nitric acid had, by parting with oxygen to the carbon of the oxide, formed carbonic acid. The carbon being thus carried off, of course the nitrogen and hydrogen of the oxide uniting produce ammoniac; which, uniting with the redundant nitric acid, composes nitrate of ammoniac; but great part of the nitrate of ammoniac was carried off in the

vapour state, exhibiting white fumes, and sublimate, as above observed.

The mode of making the experiments with the other acids was of course different from the former experiment.

Experiment II. Twenty-five grains of the above animal oxide, and half an ounce of water, were put into a bottle capable of containing three pints; a stream of oxymuriatic acid gaz, from manganese and muriatic acid, was made to pass into the bottle, and upon the charge, for twelve hours; and, for twenty-four hours more, oxymuriatic gaz kept issuing, but in smaller quantity, and circulating through the bottle. The oxide, by this time, was completely dissolved. Upon adding lime to a little of the solution of it, ammoniac was disengaged; and, upon adding sulphuric acid, there was a disengagement of oxymuriatic acid. On evaporation, however, I obtained nothing but muriate of ammoniac, with which was mixed a little manganese.

In this experiment, I could not doubt that the carbon had been carried off, in the state of carbonic acid, by the oxygen of the oxymuriatic acid; and thus ammoniac was compounded, from the union of the two remaining constituent parts of the oxide, *viz.* the nitrogen and hydrogen. The oxymuriatic acid, united to the ammoniac, parted with oxygen, and became muriatic acid during evaporation; hence, muriate of ammoniac was formed.

Experiment III. The above experiment was repeated, only the gaz was nitro-muriatic gaz, from a mixture of nitric and muriatic acids. The result was the same as in the last experiment, except that the product was a mixture of nitrate, and muriate, of ammoniac.

I made other experiments of the same kind, but their results were so nearly the same as those above related, that I shall not give an account of them. By the unexpected issue of these experiments, all my hopes of acidifying the animal oxide were exploded; but I am indebted to that pursuit, for the curious discovery of the change of the most common basis of urinary concretions, (the animal oxide,) into ammoniac and carbonic acid, by the oxygen of the above acids; which will be found extremely important, as it enables us to interpret many phenomena, in a variety of cases beside the present. It now appears, that the inflammation mentioned in one of the above experiments, (and which also happened in several others,) on evaporation of the nitric solution of the animal oxide, was from the nitrate of ammoniac, the *nitrum flammans* of the old chemists, compounded in those experiments. This inflammation takes place sometimes, on evaporation of nitric solutions, both of urinary concretions, and of urine itself evaporated to the state of soft extract, on account of the ammoniac already existing in these substances. The composition of ammoniac also explains the disappearance of the whole matter of some sorts of urinary concretions, a very small residue of black matter excepted, by repeated affusion and evaporation of nitric acid, from the solution of them in this menstruum.

It remains for me to give an account of the 96 grains of powdery matter left on the paper strainer, (*a*;) which are the insoluble portion, in lye of caustic soda, of 300 grains of urinary concretions.

1. A small portion of the insoluble matter, being exposed to flame with the blowpipe, did not turn black, nor yield any

smell of animal matter; but it became whiter, and I could just agglutinate the powder into one mass, although I was unable to render it fluid.

2. The filtrated liquid, from a little of the matter boiled in water, became very turbid and white with oxalic acid: with lime water it grew barely curdy; and it did not alter the colour of turnsole, or of violet juice.

3. The matter dissolved completely in muriatic acid, and also in nitric acid, without effervescence.

This nitric solution, having been evaporated, to carry off most of the free acid, instantly became very curdy on the addition of lime water.

It grew thick and white on adding sulphuric acid, yielding a copious precipitate of sulphate of lime. One portion of the supernatant liquor upon this precipitate, on evaporation, afforded an extract-like matter; which readily melted, as phosphoric acid does when it is mixed with a little earthy matter. To the other portion of this supernatant liquor was added liquid caustic ammoniac, producing a precipitate which afforded no sulphate of magnesia with sulphuric acid.

From these experiments it appears, that the above 96 grains of insoluble matter consisted of phosphate of lime. Accordingly, the 300 grains of urinary concretions examined, appear to contain,

	grains.
Peculiar animal oxide - - - -	175
Phosphate of lime - - - -	96
Ammoniac, (and most probably phosphoric acid united to the ammoniac,) water, and common mucilage of urine, which were not collected and weighed, by estimation	29
	<hr/> 300

I shall next relate some experiments, made in order to obtain the acid sublimate of SCHEELÉ, or lithic acid of the new system of chemistry.

100 grains of an urinary concretion, which had been previously found to contain principally the above animal oxide, were introduced into a tube $\frac{1}{4}$ of an inch wide; which was sealed at one end by fusion, and which also was fitly bent for collecting sublimate, and obtaining gaz. The sealed end was coated and exposed to fire, first to a low temperature, and gradually to a very elevated one.

1. Gaz was discharged, which had the smell of burning bone.

2. Water appeared boiling immediately over the charge, which seemed to be burning, and was turned black.

3. Gaz was discharged, of the smell of empyreumatic *liquor cornu cervi*, and about half a drachm of this liquor was in the upper part of the tube.

4. A brown sublimate of carbonate of ammoniac appeared in the cold part of the tube; but in the hotter part, near the charge, was tar-like matter, and the gaz discharged had a very offensive smell of empyreumatic animal oil, with which was mixed that of prussic acid.

The coated part of the tube was kept red hot, for some time after gaz ceased to come over.

The quantity of gaz amounted to 24 ounces, by measure: it consisted of nearly 16 ounces of carbonic acid gaz, and the rest was air, with a larger proportion of nitrogen gaz than is contained in atmospheric air.

5. There was a residue of 30 grains, almost pure carbon; and 10 grains of heavy black and brown matter, a little above the coated part of the tube. In this last mentioned matter

were many small white *spicula*. At about half an inch above the carbonaceous residue, dark gray matter had been raised, which weighed 15 grains.

This sublimed gray matter did not contain any ammoniac, nor throw down any prussiate of iron, with sulphate of iron. It reddened turnsole paper and tincture. It dissolved in caustic soda; from which solution muriatic acid precipitated nothing; for, although on dropping it into the solution milkiness appeared, the liquid soon grew clear again.

Ten grains of this sublimate dissolved in four ounces of boiling water; which being evaporated to half an ounce, there was, on cooling, a copious deposit of white *spicula*.* The sublimate had a sharp, but not sour taste. Being boiled in muriatic acid, and also in nitric, it did not dissolve at all; but remained, on evaporation to dryness, in the same state as before; and it must be particularly observed, that it left no red or pink matter, on evaporating the nitric acid from it. Sulphuric acid did not act upon it in the cold; but, when heated, it dissolved it, without effervescence, from which solution nothing was precipitated by caustic soda; on evaporating it to dryness, black fumes arose, leaving behind only a black stain. This sublimed matter did not render lime water turbid. Boiled in muriatic acid, so as to carry off all but a very little free acid, on the addition of lime water there was no turbid appearance, but milkiness ensued on adding oxalic acid.

The *spicula*, in the 10 grains of sublimate above mentioned, seemed to be of the same nature as the matter just described.

* From the deposition of these *spicula* by cooling, and from many of the following properties, they appear to be analogous to benzoic acid.

The whole of this sublimate amounted, by estimation, to 18 grains; and I apprehend it is the acid sublimate of SCHEELÉ.

The sublimate of carbonate of ammoniac amounted to 20 grains; and it was black empyreumatic animal oil which stained the tube.

This experiment was repeated, on 120 grains of a nut-brown, very light, urinary concretion. The result was not very different from that of the former experiment, except that the gaz contained a portion of hydrogen gaz. There were 30 grains of the above described *spicula*, principally mixed with carbonaceous matter: they were light, and had only a very slight sharp and bitter taste.

The experiment repeated a third time, with 80 grains of urinary concretion, afforded 15 grains of the white *spicula* above described, mixed with carbonaceous matter. These I found did dissolve in a large proportion of muriatic acid; which solution yielded them, on evaporation, in the same state as before. Under the flame applied by the blowpipe, they first melted, and then evaporated, without any smell; leaving a slight black mark. Turnsole was reddened by these *spicula*.

In a fourth experiment, I found the white *spicula* contained in the carbonaceous matter united, on boiling, with carbonate of soda, as well as with caustic soda; but, as before, muriatic acid precipitated nothing from the solution. These *spicula* could not be dissolved in nitric acid; nor did the solution of them in water become turbid with oxalic acid. Their taste was, as before, rather bitter and sharp than sour. A very suffocating smell issued forth, on breaking the tube used in this experiment, but it was not from sulphur, nor from prussic acid.

These experiments afford evidence of the wide difference between the animal oxide above described and the acid sublimate of SCHEELE.*

If this conclusion be allowed to be just, it will be necessary to give a name to this urinary animal oxide. Agreeably to the principles of the new chemical nomenclature, the name should be *Lithic oxide*. But the term *litbic* is a gross solecism; and I trust that philological critics will find the name *ouric* or *uric oxide* perfectly appropriate; for, if it be thought objectionable, on account of the existence of the matter in arthritic as well as urinary concretions, still philology will allow its admission, as in other similar cases, κατ' ἐξοχην; it being found in greater abundance, by far, in the urinary passages than in other situations, and therefore falling under common observation, as an ingredient of the urine. If, however, the term lithic oxide, or any other denomination, shall obtain acceptance, I shall very willingly adopt it.

It requires no sagacity, in a person acquainted with the facts of the preceding experiments, to perceive that they are applicable to a variety of uses in chemical investigation, and in the practice of physic. The latter I of course take no notice of in this place; but, relative to the former uses, I shall particularly point out, that we are now able not only to detect, in the easiest manner, the *presence* of the minutest proportion of the above animal oxide in urinary concretions, and also in other substances, but even to determine its *proportion* to the other constituent parts,

* From these experiments, it now appears very doubtful whether the *litbic acid* of SCHEELE exists as a constituent of urinary concretions, or is compounded, in consequence of a new arrangement taking place, of the elementary matters of the concretion, by the agency of fire; but it is demonstrated, that the urinary animal oxide is really a constituent part, and even a principal one, of almost all human urinary calculi.

in the space of a few minutes, in most cases, and in all in a very little time, without any other apparatus than nitric acid, a round bottomed matrass or glass dish, and a lamp. By this method, I have, in a general way, examined above 300 specimens of concretions, of the human subject and other animals, principally urinary ones; and also many from other parts, particularly those from the joints. For these opportunities I am beholden to several professional gentlemen; whose willingness to furnish me with specimens, I shall have much satisfaction in acknowledging on a future occasion. At present, I must acknowledge my obligations to Mr. HEAVISIDE, in whose museum I found between 700 and 800 specimens. The liberal possessor of this treasure offered me, what I could not have taken the liberty of requesting, namely, permission to break off pieces from any of the articles, for experiment. Mr. EDWARD HOWARD did me the honour to take upon himself the task of writing down the reports, and otherwise assisted me.

At this time I shall only mention,

1. That out of 200 specimens of urinary calculi, not more than six did not contain the animal oxide above described, *i. e.* about 32 out of 33 contained it.

2. That the proportion of this oxide was very different; varying from $\frac{1}{200}$ (exclusive of water,) to $\frac{199}{200}$; but, for the most part, varying between $\frac{80}{200}$ and $\frac{140}{200}$. *

3. That the common animal mucilage of urine is frequently found in concretions, in very different proportions; but is perhaps never a principal constituent part of them.

* In some urinary concretions, the interior part contained this oxide, and the exterior part had none of it. On the contrary, in other urinary concretions, the exterior part contained it, and the interior part did not.

4. That the above animal oxide was not found in the urinary concretions, or any other concretions, of any animal but the human kind.

5. That this animal oxide was found also in human arthritic calculi, but not in those of the teeth, stomach, intestines, lungs, brain, &c.

P. S. I think proper to subjoin a few experiments, made after the preceding paper was written, which afford evidence of the truth of some of my conclusions, and enable us to explain several properties of animal concretions.

I. On an Urinary Concretion from a Dog.

This calculus may be said to be a great curiosity, for it is probably the only specimen in London. I owe the opportunity of examining it to Mr. H. LEIGH THOMAS, who met with it in the course of his dissections; and therefore we have unquestionable authority, that the concretion was really from the urinary bladder of a dog. It is worthy to be noticed, that the animal appeared to be in perfect health.

This concretion is of an oval figure; is three inches and three quarters in length, and three inches in breadth; is white as chalk; its surface is rough and uneven. Being sawed through longitudinally, no nucleus was found, nor was it laminated, but near the centre it was radiated, and contained shining *spicula*. In other parts it was, for the most part, compact and uniform in its texture. It weighed nearly ten ounces and a half. Its specific gravity was found to be greater than that of human urinary concretions, in general; which I have learned by experiments is also the case with urinary and intestinal

concretions of other brute animals, especially with those of the horse.

The specific gravity of the present calculus was 1,7.

That of one from the urinary bladder of the human subject, of the sort called mulberry calculus, and which consisted almost entirely of uric oxide, was 1,609.

That of another human urinary concretion, of the same composition as the former, but quite smooth, extracted by Mr. FORD, was 1,571.

1. The present calculus of the dog had no taste, nor smell, till exposed to fire.

2. Under the blowpipe it first became black, and emitted the smell of common animal matter; it next smelt strongly of empyreumatic *liquor cornu cervi*; and, after burning some time, became inodorous, and white, and readily melted, like superphosphate of lime.

3. On trituration with lye of caustic soda, there was a copious discharge of ammoniac.

4. It dissolved, on boiling in nitric acid: the solution was clear and colourless; and, on evaporation to dryness, left a residue of *white bitter matter*, which, under the blowpipe emitted, weakly, the smell of animal matter.

5. Upon distilling a mixture of 150 grains of this concretion pulverized and two pints and a half of pure water, to three ounces, the distilled liquid was found to contain nothing but a little ammoniac. The three ounces of residuary liquid, being filtered and evaporated, yielded 20 grains of phosphate of ammoniac, with a little animal matter; and the residuary undissolved matter amounted to 67 grains.

6. These 67 grains, being triturated with four ounces of caustic

soda lye, discharged very little ammoniac. On distilling this mixture to one ounce, a very small proportion only of ammoniac was found in the distilled liquid. The residuary ounce of alkaline liquid was filtrated, and mixed with the water of elutriation of the undissolved matter. One half of those liquids, on evaporation to dryness, afforded a dark brown matter, amounting to 20 grains, which consisted of phosphate of lime and animal matter. To the other half of the alkaline liquids was gradually added muriatic acid, which occasioned a deposit, in small proportion, of matter that dissolved in nitric acid, but which, on evaporation to dryness, left behind only a brownish matter, consisting of phosphate of lime and animal matter.

7. The residuary insoluble substance in caustic lye, (6.) under the blowpipe, first turned black, and then grew white, but could not be melted.

By diluted sulphuric acid it was decomposed. On the addition of nitrate of mercury, to the filtrated liquid, it yielded phosphate of mercury; and, with oxalic acid, it afforded oxalate of lime; but no sulphate of magnesia was found remaining after these precipitations were produced.

These experiments fully demonstrate, that the above concretion of a dog contained none of the uric or lithic oxide above described, but that it consisted, principally at least, of phosphate of lime, phosphate of ammoniac, and animal matter.

The present instance leads me to explain the reason of the fusibility of calculi. This is demonstrated, by the above experiments, to depend upon the discharge and decomposition of the ammoniac of the phosphate of ammoniac, during the burning away of the animal matter; hence the residuary phosphoric

acid readily fuses, and, uniting to the phosphate of lime, composes superphosphate of lime, a very fusible substance.

The phosphate of ammoniac being dissolved out by water, or caustic alkaline lye, the remaining matter is infusible, being phosphate of lime.

A very hard, brittle, and blackish intestinal calculus of a dog, from Mr. WILSON, was found to be of greater specific gravity than human urinary calculi, and to have the same composition as that of the dog above described.

This also was found to be the composition of a white, smooth, round, intestinal calculus of a horse, the specific gravity of which was 1,791.

The same composition was discovered, on examining a very hard, gray, brittle, laminated, quadrilateral concretion, said to be from the urinary bladder, but which, I think, was more probably from the intestines, of a horse.

II. *On a Calculus from the urinary Bladder of a Rabbit.*

This is also a curiosity, being the only instance I have seen. I am likewise indebted to Mr. THOMAS for this specimen, which he very kindly sent me, fitted up as a preparation, included in the bladder itself. Mr. THOMAS found this concretion, on dissecting a perfectly healthy and very fat rabbit.

This specimen is spherical, and of the size of a small nutmeg. It is of a dark brown colour, has a smooth surface, is hard, brittle, and heavy. When broken, it appeared to consist of concentric laminæ. Its specific gravity was 2.

1. Under the blowpipe it grew black, and emitted the smell of animal matter while burning; at last it ceased to emit any

smell; and, urged with the intensest fire, showed no signs of fusibility.

2. It readily dissolved, with effervescence, like marble, in both muriatic and nitric acids, giving clear solutions.

3. The nitric solution (2.) being evaporated partly to dryness, and partly to the consistence of extract, the dry residuary matter was white; and the extract-like matter, which was bitter, could not be fused under the blowpipe; but, when brought to the state of a powder, the particles of it were made to cohere loosely together into one mass.

4. On dropping sulphuric acid into the muriatic solution, (2.) turbidness, and a copious white precipitation, immediately ensued, from the composition of sulphate of lime.

From these experiments it is warrantable to conclude, that the above urinary calculus of a rabbit consisted principally of carbonate of lime and common animal matter, with, perhaps, a very small proportion of phosphoric acid: it certainly contained no uric oxide.

I examined, in the same manner, a concretion which was said to be from the stomach of a monkey; but I have not evidence of its origin equally satisfactory as that of the two last calculi. Its composition was found to be similar to that of the calculus of the rabbit, *viz.* carbonate of lime and animal matter. Its obvious properties were also the same; it was of the size of the largest nutmeg.

III. *On urinary Concretions of the Horse.*

I examined several specimens in cabinets, said to be vesical calculi of the horse, and found none of them to contain the uric oxide above described; but that they consisted (as well

as the calculi from the stomach and intestines of the same animal) of phosphate of lime, phosphate of ammoniac, and common animal matter, which melted like superphosphate of lime, after burning away the animal matter and ammoniac. As these, and some other experiments, seemed to concur in establishing an important truth, I thought it necessary to examine an urinary concretion of a horse, which, from its figure and size, was unquestionably from the kidney of that animal; for I have found by experience, that one cannot depend entirely on the accounts in cabinets, nor indeed, sometimes, on the assertions of persons who collect specimens.

1. This concretion, which Dr. BAILLIE was so good as to give me, was of a blackish colour, was very brittle and hard, and had no smell or taste. It felt heavier than human urinary calculi.

2. Under the blowpipe it became quite black, and emitted the smell, weakly, of common animal matter. It was reduced very little in quantity, and showed no appearances of fusibility, after being exposed for a considerable time to the most intense fire of the blowpipe.

3. Muriatic acid dissolved this concretion, with effervescence, yielding a clear solution; which, on evaporation to dryness, left a black and bitter residue.

4. A little of the residue (3.) being boiled in pure water, to the filtrated liquor superoxalate of potash was added; which occasioned a very turbid appearance, and copious white precipitation.

5. Nitric acid also readily dissolved this concretion, with effervescence. The solution being evaporated, partly to dryness, and partly to the consistence of an extract, the dry residuary

matter was white and bitterish, and the extract-like part showed no signs of fusibility under the intensest fire of the blowpipe.

6. A little of the concretion, being triturated with lye of caustic soda, emitted no smell of ammoniac.

From these experiments it appears, that this calculus, like the former one from a rabbit, consists of carbonate of lime and common animal matter.

A renal calculus of a horse, in Mr. HEAVISIDE'S collection, appeared, on examination, to consist of carbonate of lime and common animal matter.

. Another specimen, however, of renal calculus of a horse, in the same collection, marked No. 3. was found to consist of phosphate of lime, phosphate of ammoniac, and common animal matter. It was fused under the blowpipe.

The specimen marked No. 8. in the same collection, which was said to be a vesical calculus of a horse, appeared to consist of the three ingredients just mentioned.

I have met with two instances of a deposit of a prodigious quantity of matter in the urinary bladder of horses, which had not crystallized, or even concreted: it amounted, in one specimen, which was given to me by Dr. MARSHALL, to several pounds weight; and in the other, which is in the possession of Mr. HOME, to about 45 pounds. Its composition was, principally, carbonate of lime and common animal matter.*

I have not found any instance of human urinary calculi of a

* Since this paper was read, Mr. BLIZARD has been so attentive as to send me another specimen of the same kind of deposit as those here mentioned. It now appears probable, that such deposits frequently take place, although I believe they have not been noticed before.

similar composition to that of the rabbit, and those of horses above described, which consist of carbonate of lime and animal matter; and I believe that human urinary calculi very rarely occur of a similar composition to those of the dog and horses above mentioned, which were found to consist of phosphate of ammoniac, phosphate of lime, and animal matter, without containing *uric oxide*.

The difference in the constitution of urinary concretions may depend on the difference of the urinary organs of different animals, on the food and drink,* and on the various diseased and healthy states of the urinary organs.

I have not found the uric oxide in the urinary concretions of any phytivorous animal; but, whether it would be formed in the human animal when nourished merely by vegetable matter, must be determined by future observations. In the mean time, it is warrantable to conclude, from analogy, that it would not, and the application of this fact to practice is obvious; but I now purposely avoid making any practical inferences, until I can, at the same time, state a number of facts I have collected, relative both to concretions and to the urine itself.

* I found the stomach-concretion called *Oriental Bezoar*, to consist merely of vegetable matter; as did the intestinal concretion of a sheep.

